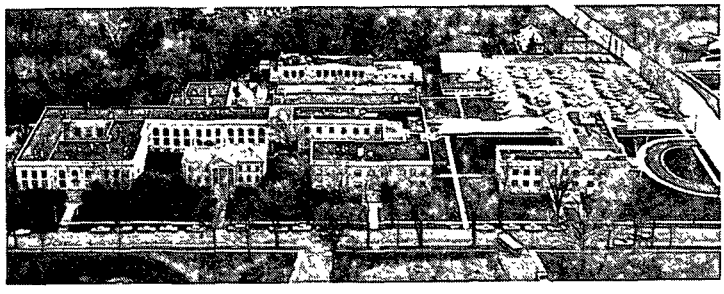

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ULTRAFILTRATION OF KRAFT BLACK LIQUOR

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Ultrafiltration of kraft black liquor

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ABSTRACT

An application of ultrafiltration to process weak black liquor (14-18% solids) is discussed. The permeate, which contains low molecular weight lignin, carboxylic acids and inorganic material, can be used as make-up black liquor in the digesters, while the concentrate can be sent to the evaporators. Data presented indicate that the boiling point rise of the concentrate is significantly lower than that of the feed liquor.

Ultrafiltration permeate flux rates are limited by concentration polarization caused by the accumulation of retained solute material at the membrane surface. Gel formation was not indicated by the experimental results. Evidence of flux limitation by solute adsorption was found.

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Introduction

The kraft recovery process is both capital and energy intensive. It is often a stumbling block when an increase in pulp production is desired. Incentives therefore exist for improving the recovery process in terms of energy consumption, throughput, and capital investment (1). Treatment of kraft black liquor by ultrafiltration may be a promising way to achieve these improvements.

Kraft lignin has potentially valuable uses as a chemical feedstock, but it is currently underutilized. In 1984, only 35,000 tons (0.2%) of the estimated 20 million tons of kraft lignin was isolated from kraft black liquor and marketed; the balance was burned in recovery furnaces (2). Economic considerations dictate that the chemical value of the lignin must outweigh the additional costs for lignin removal and auxiliary fuel to maintain the mill energy balance. Lignin removal might be considered in a pulp mill bottlenecked by inadequate firing capacity in the recovery boiler.

Lignin is present with a broad distribution of molecular weights, from monomeric products to large molecules with molecular weight greater than 50,000 (3). It is commonly removed from KBL by acid precipitation. However, recently there has been interest in using ultrafiltration (UF) for lignin separation. UF is a membrane process that is recognized as an effective and energy-efficient method for removal of moderate to high molecular weight solutes from solutions. It does not require any additional chemicals and with appropriate membranes can give narrower molecular weight fractions.

Applications of Ultrafiltration (UF)

Alkali (kraft) lignin can be used as an extender for phenol in phenol-formaldehyde resins used in plywood and chipboard manufacture. Forss and Fuhrmann (4,5)

developed the adhesive Karatex, a mixture of phenol-formaldehyde resin and lignosulfonates or alkali lignin fractionated from their respective pulping liquors by ultrafiltration. A concentrated product of approximately 90% pure alkali lignin is obtained when make-up water is added to replace the feed volume lost as permeate. Thus far, a 40% replacement of phenol has been achieved without any reduction in plywood strength properties. A commercial plant has been installed in Finland with an annual capacity of 2000 tons of purified kraft lignin (6).

Woerner (7) considered UF to partially concentrate weak black liquor or produce high molecular weight lignin. It was found that lignin rejection increased when pressure was increased or pH was decreased. The molecular weight distribution of lignin in the permeate shifted to higher molecular weights with increased pH and decreased pressure. The variation of rejection with pH was explained by the reversible association of lignin molecules after protonation of the phenolic hydroxyl group.

Hill (8) studied the use of UF to reduce KBL viscosity and ultimately improve evaporator efficiency. Mill and synthetic black liquors (mixtures of mill liquors) at 16-18% total dissolved solids (TDS) were used. Relatively open membranes were employed, 20,000-500,000 molecular weight cut-off (MWCO), to remove high molecular weight lignin. When approximately 80-90% of the feed liquor was recovered as permeate, lignin and TDS concentrations in the permeate were typically reduced by 15 and 7%, respectively, as compared to the feed, and the permeate viscosity was reduced by 30-40%. It was also found that polyvalent ions that contribute to evaporator scaling were disproportionately concentrated in the retained solutions, presumably bound by high molecular weight lignin.

Kirkman et al. (9) examined the economics of ultrafiltering 10% of the weak black liquor to remove lignin in a recovery furnace-limited mill. They presented a preliminary design estimate with the aid of computer simulation. It was concluded that reasonable returns on investment could be achieved by elimination of the bottleneck and production and marketing of high molecular weight kraft lignin.

Other benefits could be realized by treating weak KBL (14-18% solids) with ultrafiltration. The permeate from weak KBL ultrafiltration could be used as make-up liquor in the digesters. If a low MWCO membrane is used, the organic content of the permeate will be significantly reduced with respect to the feed, creating an improved make-up liquor. The concentrate can be sent to the evaporators.

One of the evaporator operating parameters that determines the final moisture content of KBL fired to the recovery furnace is the boiling point rise (BPR). BPR is defined as the difference between the boiling temperature of black liquor and that of pure water at the same pressure. For an ideal solution, the BPR is directly proportional to the molality. Therefore, at a given solids content the BPR increases with decreases in the average molecular weight of the dissolved solids.

Hill (8) found that sodium, potassium, and sulfur were concentrated in the permeate from weak KBL ultrafiltration. A reduction in the inorganic content of weak KBL to the evaporators could reduce the BPR. If the BPR could be reduced 2°F per effect, the resulting increase in throughput could be as high as 10% (10). One of the objectives of this study was to determine if UF could reduce the BPR of weak KBL.

Flux Decline and Limitation

Permeate flux decreases in UF as a direct result of concentration polarization. The operating pressure must be increased to maintain the flux. Fouled membranes must be washed periodically to restore the original flux rates.

Blatt et al. (11) conducted an in-depth study of the UF of macromolecular solutions. They observed that as the operating pressure was increased, the permeate flux at first increases, but eventually approaches a value that is pressure-independent. It was postulated that the pressure independence could be caused by the formation of a gel layer at the membrane surface when the solute concentration approaches the solubility limit.

Trettin and Doshi (12) reasoned that in the absence of a gel layer, a pressure-independent permeate flux could be caused by increased osmotic pressure of the solution near the membrane surface. Increasing the pressure can increase the solute concentration at the membrane surface to the point where osmotic pressure could be quite significant. Thus, a pressure increase can cause a proportional increase in the osmotic pressure such that the driving force ($\Delta P - \Delta \pi$) remains constant.

A pressure independent flux could be caused by other mechanisms, such as interactions between the solute and membrane. Solute can be adsorbed on the membrane surface, block the membrane pores, or deposit within the pore structure to reduce the permeate flux. Solute adsorption can affect the permeation rate in opposite directions (13). Adsorption will result in lower solute concentrations near the membrane surface. If osmotic pressure is significant and gel formation has not occurred, the effective driving force ($\Delta P - \Delta \pi$) will increase. However, the contribution of the hydraulic resistance of the adsorbed solute to the total filtration resistance will act to reduce the flux.

Woerner (7) concluded from flux decline and washing experiments that lignin is the major source of flux decline in KBL ultrafiltration. Steady-state permeate flux data were then fitted to an approximate boundary layer diffusion model which assumes complete rejection of lignin and lignin gel formation. It was concluded that a lignin gel concentration of 320 g/L fits the data within ± 10% error, independent of pH, temperature, pressure, membrane pore size, lignin to solids ratio, and wood source. There is some doubt as to whether the flux was gel-limited, since incomplete rejection was observed and rejection varied with pH and pressure.

Hill (8) found that the rejection of lignin actually increased when membranes of > 50,000 MWCO were used. This was attributed to the formation of a gel layer on the membrane which acted as a membrane with a MWCO between 20,000 and 50,000. However, Hill chose operating conditions where the flux rate was increasing with pressure; thus, it is unlikely that gel formation was indicated. Other mechanisms, such as adsorption of lignin on the membrane or pore construction caused by compaction of the membrane at higher pressures may explain the data.

A fundamental understanding of the mechanism of flux decline and limitation in KBL ultrafiltration is necessary if the process is to be optimized. In light of the previous work discussed, a second objective of this study was to determine the mechanism of permeate flux decline in KBL ultrafiltration.

Results and Discussion

BPR Reduction

Sixteen percent solids KBL was ultrafiltered through a 20,000 MWCO membrane until 25% of the feed was recovered as 12.5% solids permeate. A transmembrane pressure drop of 50 psig (345 kPa) and a feed liquor temperature of approximately 77°F (25°C) were maintained. As shown in Fig. 1, the boiling point rise reduction is approximately 0.5°F at 16% solids, and the difference steadily increases to about 3°F at 49% solids. When the same feed liquor was ultrafiltered to 50% recovery, the BPR reduction was nearly identical. This seems to indicate that the components that produce the BPR reduction are removed early in the UF process.

(Figure 1 here)

If sodium, potassium, and sulfur are concentrated in the permeate as reported by Hill (8), it seems reasonable to expect that the active alkali ($NaOH + Na_2S$) would also be concentrated. An increase in active alkali would make the permeate even more attractive as a make-up liquor. However, the results of an analysis for active alkali in the feed and fractionated liquors were inconclusive.

Flux Decline and Limitation

Gel/Osmotic Pressure - Limiting Case

The method of data analysis outlined by Trettin and Doshi (12) was followed to determine if the permeate flux is limited by gel formation or osmotic pressure. The model can be used to predict the solution concentration near the membrane

surface from cumulative permeate volume versus time measurements and knowledge of the feed and permeate concentration if the solute diffusion coefficient is known.

The assumptions made in the model are as follows:

1. The convective flux of solute to the membrane is balanced by back-diffusion of solute.
2. The solute diffusion coefficient is constant.
3. The concentration of the solution near the membrane surface reaches a constant limiting value at large time.

If gel-limited UF is indicated, the concentration of lignin near the membrane surface (wall concentration) will reach the same limiting value independent on the transmembrane pressure, at the same feed conditions (pH, feed concentration, etc.). If osmotic pressure is limiting the ultrafiltration process, the wall concentration will reach the same limiting value independent of the feed concentration, at the same applied pressure and other feed conditions.

Model kraft lignin solutions (Indulin AT in NaOH) were ultrafiltered through 10,000 MWCO membranes at transmembrane pressures of 483-1380 kPa (70-200 psig), pH 10.2-12.5, and T = 21°C. Pertinent data are presented in Table I. A diffusion coefficient for kraft lignin in KBL was calculated from a correlation developed by Burazin (14). The value 1.84×10^{-6} cm^2/sec was used to calculate the theoretical wall concentrations, Cw, also shown in Table I.

(Table I here)

If a gel layer of lignin forms at the solute solubility limit, then it should form a coherent, uniform structure that is relatively incompressible.

The concentration of a hypothetical gel would not be expected to vary by more than a few percent with an increase in pressure. If this mental picture of a gel is correct, then gel-limited UF is not indicated, because the wall concentration varies a great deal with transmembrane pressure (at constant feed conditions), as shown in Table I.

Osmotic pressure may contribute to flux limitation. The wall concentrations at pH 11.3 and different feed concentrations differ by ± 20%, as shown in Table I. However, osmotic pressure cannot be the only mechanism that limits the permeate flux. Lignin rejection increases with an increase in the transmembrane pressure in KBL ultrafiltration. If osmotic pressure is the only mechanism that limits the permeate flux, then the rejection of lignin should decrease with increasing pressure, because the increased concentration polarization of lignin will increase the probability that lignin will pass through the membrane.

The diffusion coefficient used here must be considered an average value. The actual diffusion coefficient will decrease with increasing molecular weight (or molecular size) and decrease with decreasing pH due to lignin agglomeration, which will cause an increase in the average particle size. If the actual diffusion coefficient is lower than the one used here, the calculated wall concentration will be higher.

Solute Adsorption - Limiting Case

The data were then compared to the filtration model derived by Doshi (13) to describe flux limitation by solute adsorption. The assumptions used to derive the model are as follows:

1. Back diffusion of solute is negligible.
2. The permeate flux is determined mainly by the filtration resistance of the adsorbed layer.
3. The solute concentration near the membrane surface approaches the feed concentration.
4. The solute adsorption flux is inversely proportional to the square root of time.

The model can be used to predict the specific filtration resistance of the adsorbed layer. The specific filtration resistance is a function of the packing density of the material that provides the filtration resistance - the larger the packing density (or smaller the void volume), the larger the specific filtration resistance.

Trettin and Doshi (15) describe a dimensionless parameter, K, that is proportional to the ratio of the mass transfer boundary layer thickness to the adsorbed layer thickness (i.e., the ratio of diffusive flux of solute away from the membrane to the convective flux of solute to the membrane) in unstirred batch cell ultrafiltration. K is defined as follows:

$$K = \frac{\alpha \mu \ Co \ D}{\Delta P}$$

α = specific filtration resistance of adsorbed layer
μ = permeate viscosity
Co = feed concentration of solute
D = solute diffusion coefficient
ΔP = transmembrane pressure

K was calculated for the above mentioned experiments at pH 12.7 with the measured values of filtration resistance, as shown in Table II. The values of K are much less than 1, indicating that solute adsorption may be the dominating factor that limits the permeate flux and that back diffusion may be negligible.

(Table II here)

Refer again to Table II. The specific filtration resistance increases with pressure. This result may explain why lignin rejection increases with pressure in KBL ultrafiltration. This also indicates that the permeate flux in KBL ultrafiltration may be adequately described by a filtration model.

Conclusions

Preliminary results have shown that ultrafiltration can be used to lower the boiling point rise of weak kraft black liquor and consequently improve evaporator efficiency. Further work needs to be done to determine the optimum BPR reduction that can be achieved and the optimum operating conditions for this application. Additional work is needed to characterize the permeate and to determine its suitability as a make-up liquor for pulping.

Permeate flux limitation in kraft black liquor ultrafiltration appears to be dominated by solute adsorption. Flux limitation by lignin gel formation was not indicated. A fundamental understanding of the mechanism of flux limitation in KBL ultrafiltration will be helpful in optimizing and modeling the process. Further work needs to be done to gain a better understanding of the adsorption process and to determine the extent of any contribution of osmotic pressure to flux limitation.

Experimental

Black Liquor

Synthetic black liquor was made with Indulin AT and sodium hydroxide. Indulin AT is a pine kraft lignin produced by acid precipitation of KBL and is available in powdered form. pH adjustment was made with sodium hydroxide pellets or concentrated sulfuric acid.

One hundred percent softwood, 50% solids black liquor was obtained from Thilmany Pulp and Paper Mill. After dilution with distilled water, the liquor was prefiltered through quantitative filter paper to remove small amounts of residual pulp and particulate material.

All liquor was stored in a cold room. Samples were removed from refrigeration at least six hours before use to bring them to room temperature. Care was taken to avoid significant air entrainment in the samples which would cause foaming.

Concentration Measurement

Black liquor solids concentrations were determined gravimetrically by oven drying at 105°C. It was felt that solids concentration would give a good estimate of lignin rejection because the rejection of other liquor components is negligible.

Boiling Point Rise Measurements

Three hundred mL of liquor were refluxed in a 500 mL Erlenmeyer flask. Liquor temperature was measured by an iron-constantan thermocouple. Vapor temperature was measured with a mercury thermometer. Vapor was condensed in a water-cooled condenser. At equilibrium, the BPR was calculated from the difference in liquor

and vapor temperatures. Solids concentration changes were made by collecting condensate in a graduated cylinder. Concentration changes were monitored by back-calculating the solids concentration with the collected condensate volume.

Continuous UF Experiments

The apparatus used in the BPR reduction experiments is shown in Fig. 2. A Dorr-Oliver thin-channel UF cell was used. The cell is made of Plexiglas and has a rectangular channel with the dimensions 12.0 x 3.0 x 3.8 cm. Twenty thousand MWCO polysulfone membranes supplied by Osmonics, Inc., were used. The membranes, with an effective area of 40 cm^2, were supported by blotter paper.

Liquor was pumped from and recirculated to a nitrogen-pressurized reservoir. Piping was 1/2-inch 304 stainless steel. A centrifugal pump with a 1/2 hp motor was used to transfer the liquor from the tank to the cell. Two liters of mill liquor diluted to approximately 16% solids was used as feed. Inlet feed pressures were maintained at 50 psig. Liquor temperature was maintained at 24-27°C by a double-pipe water-cooled heat exchanger.

Unstirred Batch Cell Experiments

Experiments to investigate the flux limitation mechanism were carried out in two unstirred batch cells manufactured by the Gelman Filter Company, as shown in Fig. 3. Each cell has a volume of 230 mL and is composed of three parts: a cylindrical cell and two screen caps made of stainless steel. The bottom cap contains a support screen over which a UF membrane was fitted and secured with a Teflon gasket. The cells were pressurized through fittings in the top screw cap with nitrogen and clamped to a support structure to prevent excessive vibration.

Cell pressure was varied between 483 and 1380 kPa (70-200 psig). Experiments were performed at 21.0 ± 1.0°C in a room with temperature control. Ten

thousand MWCO polysulfone membranes supplied by Amicon Corporation were used. The effective membrane area was 13 cm^2. A fresh membrane and 200 mL of feed liquor were used in each experiment.

Total permeate volume was collected and measured in two 50-mL graduated cylinders. The batch cell geometry was such that a correction of 2 mL had to be added to account for permeate trapped in the cell.

For the unstirred batch cell, Trettin and Doshi (12) showed that at large time the collected permeate volume is proportional to the square root of time, regardless of the nature of the solution. If ΔV_i represents the permeate volume collected between time $t = 0$ and $t = T_i$, the following relationship between data points can be derived.

$$\frac{\Delta V_2 - \Delta V_1}{\Delta V_3 - \Delta V_1} = \frac{T_2^{1/2} - T_1^{1/2}}{T_3^{1/2} - T_1^{1/2}}$$

Permeate volume measurement times were chosen such that $T_2 = 2T_1$, and $T_3 = 4T_1$, giving

$$\frac{\Delta V_2 - \Delta V_1}{\Delta V_3 - \Delta V_1} = 0.4142$$

Data acceptability limits were set at ± 3% of the 0.4142 value. Over 95% of the data fell within this range. Permeate was collected for as long as 24 hours in some experiments. The data were then analyzed with the models developed by Trettin and Doshi (12) and Doshi (13) to predict the flux-limiting mechanism.

Acknowledgments

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I. Batch cell UF data

Lignin Concentration			Transmembrane Pressure		Theoretical Wall Concentration
Feed Co g/cc	Permeate Cp g/cc	pH	ΔP kPa (psig)	Rejection 1 - Cp/Co	Cw g/cc
0.0359	0.0243	11.3	483 (70)	0.323	0.246
0.0359	0.0174	11.3	896 (130)	0.515	0.341
0.0359	0.0155	11.3	1380 (200)	0.680	0.479
0.0181	0.0114	11.3	483 (70)	0.370	0.208
0.0181	0.0080	11.3	896 (130)	0.558	0.446
0.0181	0.0079	11.3	1380 (200)	0.563	0.425
0.0353	0.0344	12.5	483 (70)	0.025	0.063
0.0353	0.0311	12.5	896 (130)	0.119	0.135
0.0353	0.0289	12.5	1380 (200)	0.181	0.208
0.0361	0.0130	10.2	483 (70)	0.639	0.280
0.0361	0.0111	10.2	896 (130)	0.692	0.354
0.0361	0.0092	10.2	1380 (200)	0.745	0.419

II. Application of the filtration model

Mill Liquor: pH - 12.7, Co = 0.0516 g/cc; μ = 0.98 centipoise
$D = 1.84 \times 10^{-6}$ cm^2/sec

$$K = \frac{\alpha . \mu . Co . D}{\Delta P}$$

Transmembrane Pressure ΔP kPa (psig)	Specific Filtration Resistance $\alpha \times 10^{-14}$ cm/g	Dimensionless Parameter $K \times 10^2$
480 (70)	8.3	1.6
900 (130)	10.8	1.1
1380 (200)	15.7	1.1

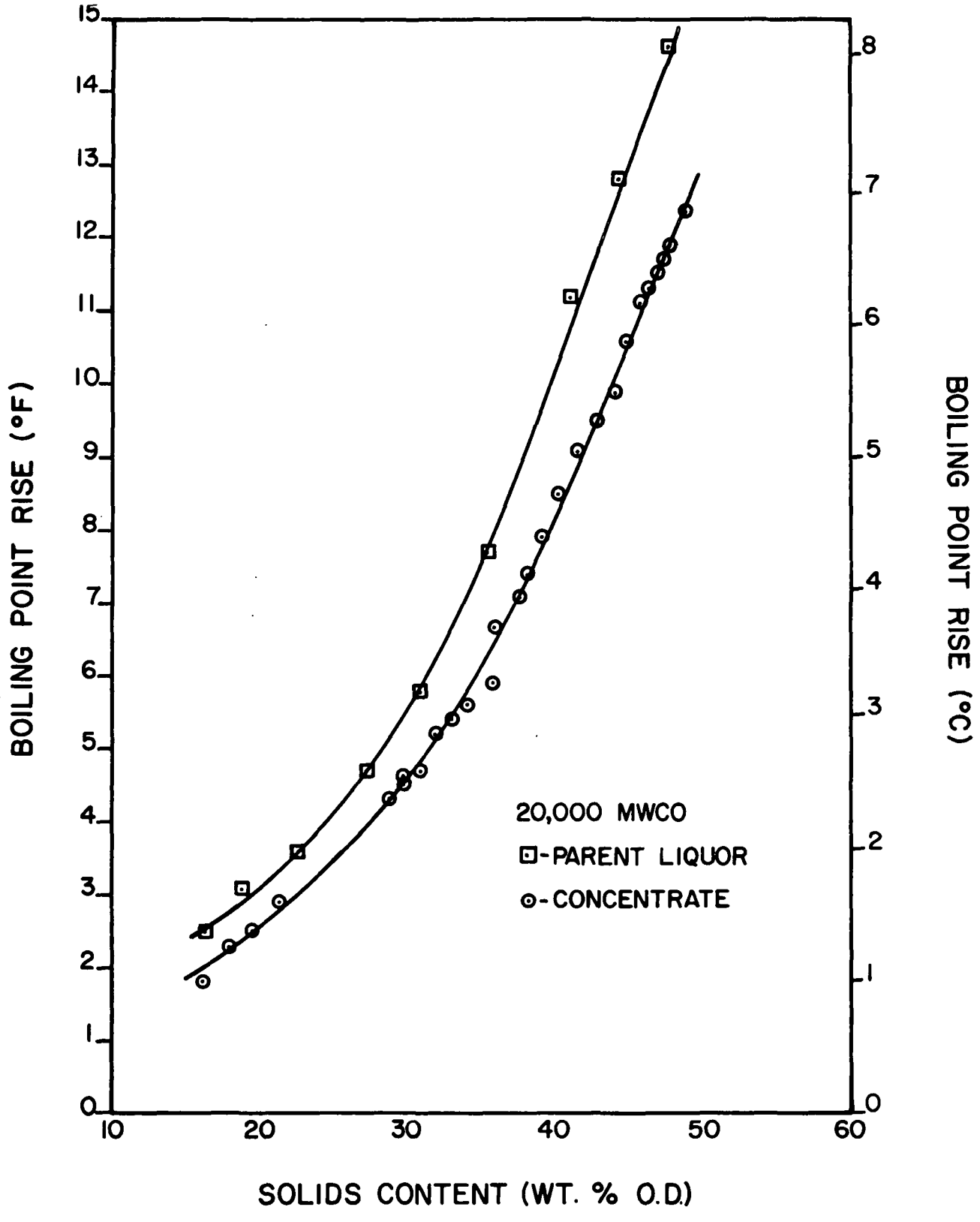

Figure 1. Typical BPR reduction results.

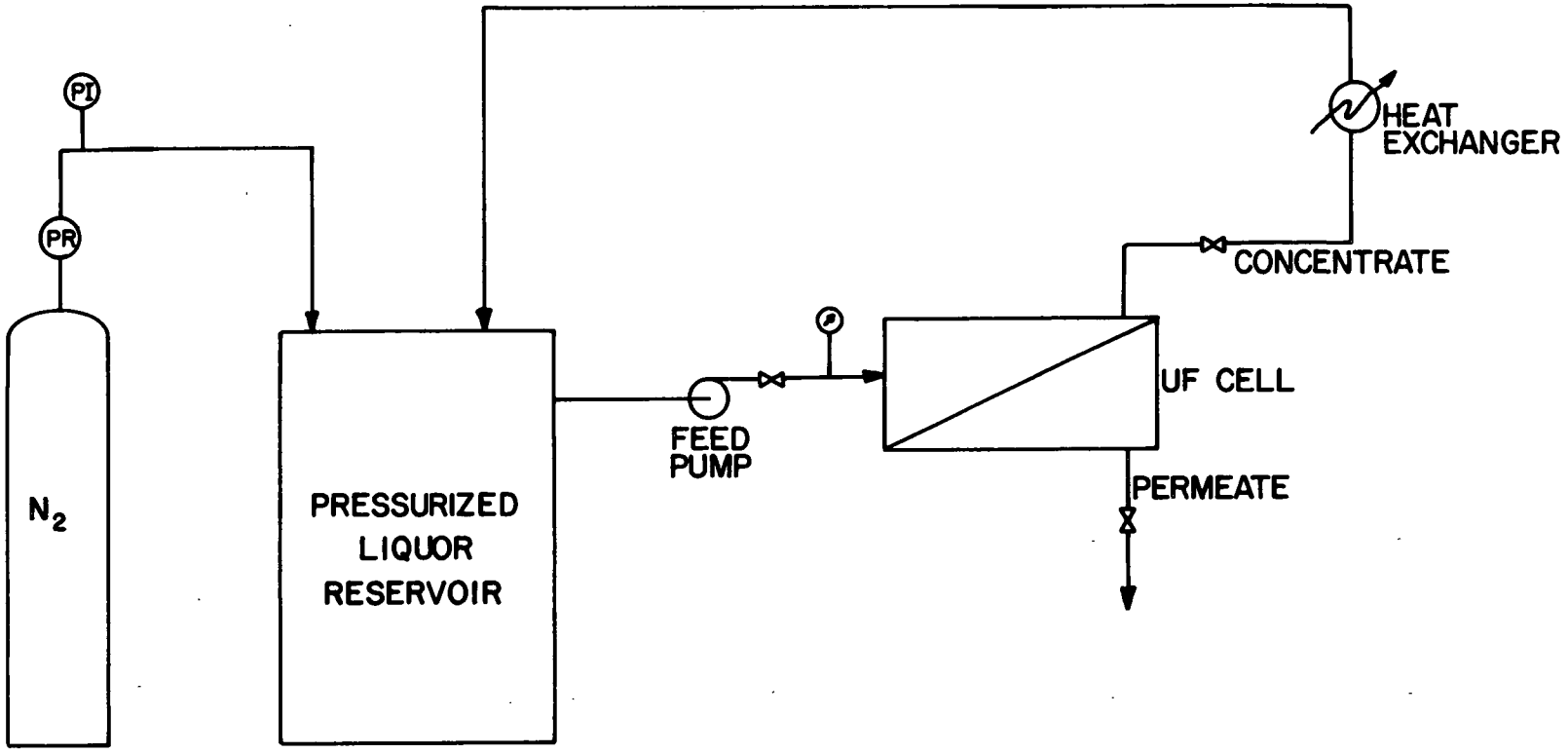

Figure 2. Continuous UF apparatus.

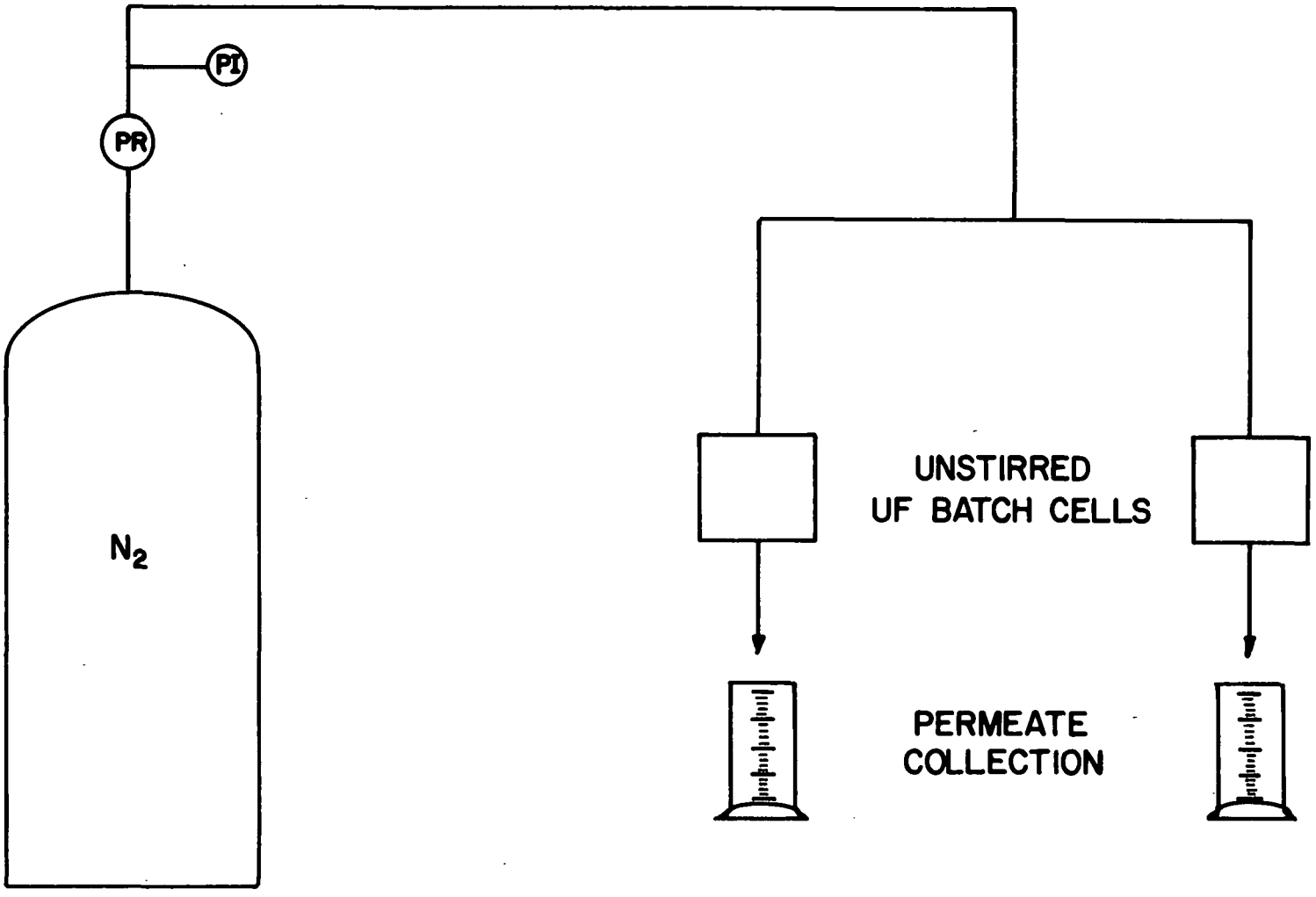

Figure 3. Unstirred batch cell apparatus.